LXI.—*The Reaction between Grignard Reagents and* 10-*Chlorophenoxarsine or* 10-*Chloro*-5 : 10-*dihydrophenarsazine.*

By John Alfred Aeschlimann.

The method of preparing 10-ethylphenoxarsine by heating 10-chlorophenoxarsine with magnesium ethyl bromide described by the author (J., 1925, **127**, 813) has been extended to the 10-*methyl* and 10-*phenyl* compounds, derivatives of which have been prepared. 10-Methylphenoxarsine can be readily obtained by performing the Grignard reaction in the cold as described by Roberts and Turner (J., 1926, 1210), who, although they did not isolate any arsine, claimed that their method is of general application. That this is not the case follows from the experimental results described below, and agrees with the previous work of Lewis, Lowry, and Bergheim (*J. Amer. Chem. Soc.*, 1921, **43**, 890), who failed to isolate either the phenyl- or the ethyl-phenoxarsine under similar conditions, but mistook for the latter a compound, m. p. 218°, which was probably phenoxarsinic acid, m. p. 219°, as this can be isolated by allowing the oxide formed in the reaction to oxidise in air. Of the above three arsines, only the phenyl derivative is crystalline.

In several attempts to obtain 10-phenylphenoxarsine by the condensation of diphenyl ether with phenyldichloroarsine in presence of aluminium chloride, only 10-chlorophenoxarsine was obtained. This result is analogous to that obtained by Burton and Gibson (J., 1926, 465) in the condensation of diphenylamine and phenyldichloroarsine, although they used no catalyst to facilitate the decomposition of the dichloroarsine to arsenious chloride. 10-Chlorophenoxarsine does not give 10-phenylphenoxarsine on being heated with benzene and aluminium chloride.

10-Chloro-5 : 10-dihydrophenarsazine reacts with two molecules of the respective Grignard reagents to give 10-*methyl*-5 : 10-*dihydrophenarsazine*, 10-*ethyl*-5 : 10-*dihydrophenarsazine*, and 10-*phenyl*-5 : 10-*dihydrophenarsazine*, hydrocarbons also being formed owing to the presence of the NH-group. When the reaction mixture is cooled during addition of the chloroarsine, the formation of hydrocarbon does not take place and the heavy oil which separates from the ethereal solution should contain the : NH(MgI)R group. Treatment of this with methyl iodide, however, does not produce 5 : 10-dimethyl-5 : 10-dihydrophenarsazine, but 10 : 10-*dimethyl*-5 : 10-*dihydrophenoxarsonium iodide,* which is also the product when the methylation of 10-methyl-5 : 10-dihydrophenarsazine is attempted under various conditions. The latter compound, unlike 10-chloro-5 : 10-dihydrophenarsazine (Wieland and Rheinheimer, *Annalen*, 1921, **423**, 1), which loses hydrogen chloride from the 5 : 10-positions to produce phenarsazine when heated in a vacuum, loses methyl iodide under these conditions and re-forms 10-methyl-5 : 10-dihydrophenarsazine. The methyldihydrophenarsazine combines with ethyl iodide, and the ethyldihydrophenarsazine with methyl iodide, to form the same 10-*methyl* : 10-*ethyl*-5 : 10-*dihydrophenarsazonium iodide*. The formation of the arsonium rather than the ammonium compound by addition of alkyl iodide recalls the ease of formation of sulphonium compounds from the similarly constituted di-*p*-nitrodiphenylamine sulphoxide (Smiles and Hilditch, J., 1908, **93**, 145, 1687).

The observation of Turner, Sheppard, and Bolton (J., 1925, **127**, 547), that diphenylene disulphide is formed when a mixture of arsenic trichloride and diphenyl sulphide is heated with aluminium chloride, has been extended to the reaction between arsenic trichloride or phenyldichloroarsine and the double compound $(C_6H_5)_2S,AlCl_3$ (Böeseken, *Rec. trav. chim.*, 1905, **24**, 219). Equimolecular quantities of triphenylarsine, sulphur monochloride, and aluminium chloride similarly fail to produce a cyclic arsine, the product after treatment with water being triphenylarsine dihydroxide.

EXPERIMENTAL.

10-Methyl- and 10-ethyl-phenoxarsines were each prepared by the addition of 10-chlorophenoxarsine (10 g.) to the stirred Grignard reagent (2 mols.). The yields obtained after decomposition of the products as described by Roberts and Turner (*loc. cit.*) were : from MgMeI, 85%; from MgEtI, 40% (impure); from MgEtBr, 20% (impure). 10-Phenylphenoxarsine was not isolated in this way, as it was difficult to separate from unchanged chlorophenoxarsine.

10-Ethylphenoxarsine was obtained in 80% yield by heating 10 g. of 10-chlorophenoxarsine in 60 c.c. of benzene with 1½ mols. of magnesium ethyl bromide in 50 c.c. of ether for 2½ hours. When only 1¼ mols. of the Grignard reagent were used as previously described, the yield was about 70%.

10-*Methylphenoxarsine* is a colourless oil, b. p. 185°/20 mm., 198—200°/40 mm. (Found : C, 60·7; H, 4·2. $C_{13}H_{11}OAs$ requires C, 60·5; H, 4·3%).

10-*Methylphenoxarsine dihydroxide*, m. p. 94°, was obtained by dissolving the arsine in excess of hydrogen peroxide solution, evaporating the water and recrystallising the residue from benzene (Found : C, 53·7; H, 4·45. $C_{13}H_{13}O_3As$ requires C, 53·4; H, 4·45%).

It is dehydrated to the oxide when heated in a vacuum at 50° (Found: loss, 5·9. Calc. for 1 H_2O; loss, 6·1%). The hydroxide is re-formed after 12 hours' exposure of the oxide to air.

10 : 10-Dimethylphenoxarsonium iodide forms white needles which melt at 225° when slowly heated and at 220° when rapidly heated in closed or in open tubes [Found: I (Carius), 31·7. Calc.: I, 31·7%]. Roberts and Turner (*loc. cit.*) give m. p. 207°.

10-Methyl-10-ethylphenoxarsonium iodide (Aeschlimann, *loc. cit.*) is less readily formed from 10-methyl- than from 10-ethylphenoxarsine and the requisite alkyl iodide. Only the white compound was isolated in the former case.

10-*Methyl*-10-*carboxymethylphenoxarsonium bromide*, m. p. 199°, was formed on heating equimolecular quantities of 10-methylphenoxarsine and bromoacetic acid for 15 minutes at 90°, the stirred mixture gradually becoming solid. The product was washed with ether and recrystallised from alcohol, in which it was not easily soluble (Found: Br, 20·3, 20·6; equiv. by titration with alkali, 394. $C_{15}H_{14}O_3BrAs$ requires Br, 20·2%; equiv., 397).

10-*Ethylphenoxarsine sulphide* was slowly formed by the action of hydrogen sulphide on an aqueous solution of the oxide, or by addition of excess of sulphur to a solution of 10-ethylphenoxarsine in carbon disulphide. It is soluble in ether, and crystallises from alcohol in long needles, m. p. 109° (Found: S, 10·1. $C_{14}H_{13}OSAs$ requires S, 10·6%).

10-*Phenylphenoxarsine* was obtained in 75% yield by heating the Grignard reagent prepared from 15 g. of bromobenzene with 10 g. of 10-chlorophenoxarsine in benzene for 4 hours. (The reaction is incomplete after 2½ hours' heating, and the unchanged chloroarsine is difficult to remove from the product, which boils at 270°/30 mm. and solidifies slowly.) It crystallised from alcohol in colourless needles, m. p. 107° (Found: C, 66·8; H, 4·1. $C_{18}H_{13}OAs$ requires C, 67·5; H, 4·1%).

10-*Phenyl*-10-*methylphenoxarsonium iodide*, m. p. 175°, did not appear to be formed until the reactants were heated (Found: I, 27·6. $C_{19}H_{16}OIAs$ requires I, 27·5%).

10-*Phenylphenoxarsine oxide*, m. p. 184°, was formed by dehydrating the hydroxide in a vacuum at 50° (Found: C, 64·2; H, 3·8. $C_{18}H_{13}O_2As$ requires C, 64·4; H, 3·9%). The hydroxide was obtained by the action of hydrogen peroxide, or of sulphur monochloride and water (Zuckerkandl and Sinai, *Ber.*, 1921, **54**, 2484), on 10-phenylphenoxarsine. It is deliquescent, and retains 1½ mols. of water on drying to constant weight in a desiccator; it then melts at 93° (Found: loss on conversion into oxide, 7·2. Calc. for 1½H_2O: loss, 7·4%).

10-*Methyl*-5 : 10-*dihydrophenarsazine* was obtained by the addition of 14 g. of powdered 10-chloro-5 : 10-dihydrophenarsazine in three portions to the Grignard reagent (2·1 mols.) prepared from 16 g. of methyl iodide and 2·6 g. of magnesium in 50 c.c. of ether. (Usually ebullition and evolution of hydrocarbon vapours were allowed to occur, and immediate solution then took place. If, however, the reagent was cooled in a freezing mixture during the addition, gas was not evolved and two layers were formed. When this mixture was heated with methyl iodide, only the arsonium iodide and the methyl arsine were formed.) The mixture was heated for a short time to complete the reaction and then decomposed in the usual manner; the residue crystallised after evaporation of the ether from the extract. After recrystallisation from hot alcohol, the *dihydrophenarsazine* melted at 105°, and was soluble in the usual solvents except light petroleum. It was usually yellow, but formed almost colourless plates after being recrystallised several times (Found : C, 60·6; H, 4·0. $C_{13}H_{12}NAs$ requires C, 60·7; H, 4·1%).

10-*Ethyl*-5 : 10-*dihydrophenarsazine*, obtained in a similar way, melted at 75° (Found : C, 62·0; H, 5·0. $C_{14}H_{14}NAs$ requires C, 62·0; H, 5·2%).

10-*Phenyl*-5 : 10-*dihydrophenarsazine*, m. p. 142°, was less soluble in alcohol than the alkyldihydrophenarsazines, and required heating for its formation (Found : C, 68·1; H, 4·4. $C_{18}H_{14}NAs$ requires C, 67·7; H, 4·4%).

All three arsines reacted with methyl iodide to form arsonium iodides, crystallisable from hot alcohol and only slightly soluble in water. The methyl compound reacted in the cold, the others required heating. Even in presence of a large excess of methyl iodide in a sealed tube at 100°, only one molecule of the iodide took part in the reaction; a similar combination took place at the ordinary temperature.

10 : 10-*Dimethyl*-5 : 10-*dihydrophenarsazonium iodide* has m. p. 259° (slow heating), 268° (rapid heating) (Found : C, 42·1; H, 3·6; I, 31·7. $C_{14}H_{15}NIAs$ requires C, 42·2; H, 3·8; I, 32·0%).

10-*Methyl*-10-*ethyl*-5 : 10-*dihydrophenarsazonium iodide*, m. p. 236° (rapid heating), 229° (slow heating), was obtained from either the methyl or the ethyl compound and the appropriate alkyl iodide (Found : I, 30·4. $C_{15}H_{17}NIAs$ requires I, 30·7%).

10-*Phenyl*-10-*methyl*-5 : 10 *dihydrophenarsazonium iodide* has m. p. 158° (decomp.) (Found : I, 27·9. $C_{19}H_{17}NIAs$ requires I, 27·6%).

5-*Acetyl*-10-*methyl*-5 : 10-*dihydrophenarsazine*, m. p. 154°, was obtained by boiling the arsazine with an excess of acetic anhydride for 1 hour, removing the latter in a vacuum, and crystallising the product from alcohol. It is less soluble in ether than the arsazine (Found : C, 60·6 ; H, 4·5. $C_{15}H_{14}ONAs$ requires C, 60·2 ; H, 4·7%).

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